Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 69 (2015) 1551 – 1557

Energy Procedia

International Conference on Concentrating Solar Power and Chemical Energy Systems, SolarPACES 2014

Study of the stability of a selective solar absorber coating under air and high temperature conditions

O. Raccurt[a]*, A. Disdier[a], D. Bourdon[a], S. Donnola[b], A. Stollo[b] and A. Gioconia[c]

[a] *Univ. Grenoble Alpes, F-38000 Grenoble, France, CEA, LITEN, High Temperature Solar Systems Laboratory, National Institute of Solar Energy (INES), 73377 Le Bourget-du-Lac, France*

[b] *ARCHIMEDE Solar Energy SRL (ASE), Voc. Flaminia Vetus 88, V.S. Faustino, 06056 Massa Martana, Italy.*

[c] *ENEA, Lungotevere Grande Ammiraglio Thaon di Revel 76, 00196 Roma, Italy.*

Abstract

Selective solar absorber material is one of the major components in the Concentrated Solar Power (CSP) technologies. Its optical properties determine the efficiency of the energy conversion from the concentrated sun irradiation to the heat recovered by the heat transfer fluid. Development of the CSP requires costs reduction for this technology. To achieve this goal, one way is the increase of the work temperature up to 400 – 500°C or more. For economic reasons, the bankable of CSP technology requires a lifetime over 25 years for components and so for solar absorbers. The development of solar receiver, able to operate under air, instead of vacuum conditions, is a challenge to reduce the costs. Along the 25 years of a CSP plant lifetime, solar absorber material is daily exposed to high levels of stresses: high solar flux, high thermal gradient. As the oxidation is one of the main factors involved in degradation processes air stability of the absorber coating under high temperatures should be studied as it could be a critical point in the solar field maintainability in case of accidental vacuum loss. In this article we present a durability study of selective solar absorber from Archimede Solar Energy (ASE) exposed in air at high temperature (up to 500°C). The results show a good stability of this materials up to 450°C during 3000h without change of solar absorptance and emittance. An analysis of the degradation process at higher temperature is presented.

Peer review by the scientific conference committee of SolarPACES 2014 under responsibility of PSE AG

Keywords: Selective Solar Absorber, Durability, Air stability

* Corresponding author. Tel.: +33 (0)4 79 79 21 18; fax: +33 (0)4 79 62 13 74.
E-mail address: olivier.raccurt@cea.fr

Peer review by the scientific conference committee of SolarPACES 2014 under responsibility of PSE AG
doi:10.1016/j.egypro.2015.03.107

Nomenclature

α	Total solar absorptance
$\varepsilon(T)$	Total emittance at temperature T
$\rho_T(\lambda)$	Hemispherical reflectance measurement
$S(\lambda)$	Solar spectra
$B_T(\lambda)$	Black body spectra at temperature T
CSP	Concentrated Solar Power
IR	Infrared
UV	Ultraviolet
FTIR	Fourier Transform InfraRed
SEM	Scanning Electron Microscopy

1. Introduction

Selective solar absorber material is one of the major components in the Concentrated Solar Power (CSP) technologies. Its optical properties determine the efficiency of the energy conversion from the concentrated sun irradiation to the heat recovered by the heat transfer fluid. The ideal selective solar absorber should present a high solar absorptance (α>90%) and a low emissivity at the working temperature ($\varepsilon(T)$<10%) [1]. Development of the CSP requires reduction of this technology costs. To achieve this goal, one way is the increase of the work temperature up to 400 – 500°C or more for the linear technologies like parabolic trough or Fresnel solar field [1]. For economic reasons, the bankable of CSP technology requires a lifetime over 25 years for component and so for solar absorber. As solar receivers are usually maintained under vacuum as to limit convective thermal losses, the absorber coating is designed to operate without oxidative atmosphere. However, the development of solar receiver, able to operate under air, is a challenge to reduce the costs. It's also a way to lower the complexity of linear CSP (parabolic trough and Fresnel technologies). In this context, many studies are on progress to developed new selective solar absorber working at high temperature [1]. The stability under air with high temperatures for absorber coatings is so a main target for the community of CSP. Along the 25 years of a CSP plant lifetime, solar absorber material is daily exposed to high levels of stresses: high solar flux, high thermal gradient. Even though the solar receiver has been designed to operate under vacuum conditions (inside the annulus, the receiver has a proper getter material able to compensate the nominal leakage rate during 25 years expected lifetime and designed in order to assure the maintenance of an annulus pressure less than 10^{-4} mbar), in a real plant lifetime some of the receivers could operate in oxidating atmosphere essentially due to accidentally glass breakage or more generally due to unexpected vacuum loss. As the oxidation is one of the main factors involved in degradation processes, air stability of the absorber coating under high temperatures should be studied as it could give important information for solar field maintainability. Furthermore, in some applications, "naked" tubes (receivers without glass envelop directly exposed to external environment) could be used so that the investigation of the maximum temperature they can withstand for long period is an essential information. On the MATS project the absorber on the parabolic trough central is used in vacuum conditions up to 600°C. This material is stable under the ideal conditions: vacuum and maximum temperature at 550°C under operation. The presence of oxygen under the absorber tube may be possible if there is an accidental breaking of vacuum during the time of service. The ageing test in air atmosphere is a very aggressive test compared to the expected application in standard conditions.

2. Materials and method

This work has been realized in the frame of the European project MATS. The stability of a selective solar absorber coating from Archimede Solar Energy has been studied. This selective absorber is based on a technology developed by ENEA [2] using a double cermet and antireflective coating.

Optical absorptance have been measured by spectrophotometry to a Perkin Elmer Lambda 950 with an integrating sphere of 150mm and a FTIR spectrophotometer Tensor 27 from Bruker with a gold integrating sphere of 150mm. Lambda 950 is used to measure spectra between 300 and 2500nm, Tensor 27 is used to measure spectra between 2000 and 15000 nm. Optical properties (α and ε(T)) were calculated from absorptance spectra (see eq. (1) and (2)). Solar absorptance was calculated with the ASTM G173-03 reference spectra derived from SMARTS v. 2.9.2, between 280 and 2500nm. Emissivity was calculated in comparison to the black body curve at the temperature T in the range of 0.28 to 15µm. Where $\rho_T(\lambda)$ hemispherical reflectance measurement, $S(\lambda)$ solar spectra, $B_T(\lambda)$ black body spectra at temperature T [1].

$$\alpha = 1 - \int_{\lambda = 280nm}^{2500nm} \frac{\rho_T(\lambda) \times S(\lambda)}{S(\lambda)} d\lambda \quad (1)$$

$$\varepsilon(T) = \int_{\lambda = 280\,nm}^{15\,000\,nm} \frac{\rho_T(\lambda) \times B_T(\lambda)}{B_T(\lambda)} d\lambda \quad (2)$$

The sample older of two sphere has been designed for plan sample and is not adapted to measure tubes. The size of sphere port is 4 cm diameter for IR and 3 cm diameter for UV-VIS spectrophotometer. For this reason, plan samples were required for this ageing study. Figure 1 shows a photograph of samples from ASE with a size of 7.5 x 2.5cm (Fig. 2) coming for two deposition runs. Due to the smaller size of sample compare to the sphere port, two side by side samples were used for measurement to cover the port of the sphere. This configuration is a possible cause of the noise observed in the IR part of spectra (Fig 2.). A calibration of the spectrophotometer was done between the measurement after 2400h and 2900h.

Fig. 1. Photograph of sample as received from ASE.

The ageing tests have been realized at constant temperature at four temperatures: 350, 400, 450 and 500°C. Ageing test was used air circulating climatic chamber. As the available samples were only 8, to have a minimum of reproducibility two samples for each temperature have been used and 2 samples of each temperature coming from two different deposition run. One sample has been conserved as reference. Optical properties (α and ε(T)) were measured over the time. As function of degradation, SEM (scanning electronic microscopy) observation of surface sample was used to identify the degradation of materials.

3. Results

Figure 2 shows the optical reflectance spectra between 300nm to 20000nm compared to the normalized solar spectra and the black body emittance spectra at 100, 300 and 450°C.

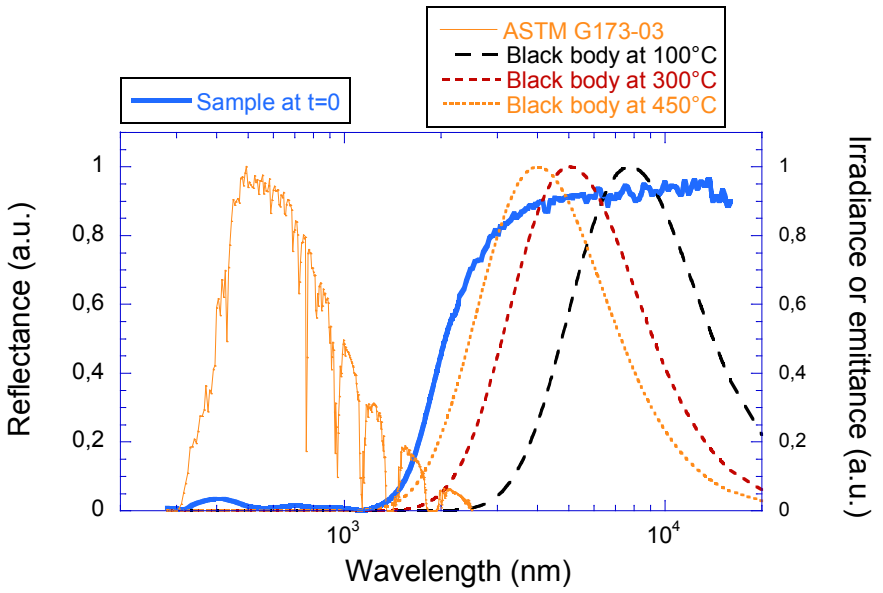

Fig. 2. Reflectance vs wavelength for ASE absorber coating before ageing compared to the normalized solar (ASTM G173-03) and blackbody spectra at 100, 300 and 450°C.

Figure 3 shows the relative variation of solar absorptance $\Delta\alpha$ (eq. (3)) and emittance at 450°C $\Delta\varepsilon_{T=450°C}$ (eq. (4)) as function of time for each temperature test. At the beginning of the test, during the first 750h, a little decrease of solar absorptance around 0.5% was observed for all samples.

$$\Delta\alpha=\alpha(t)-\alpha(0) \quad (3)$$

$$\Delta\varepsilon_{T=450°C}=\varepsilon_{T=450°C}(t)-\varepsilon_{T=450°C}(0) \quad (4)$$

After 750h we observe a stabilization of the value excepted for samples at 500°C where the absorptance decreases continuously. A good stability of the optical properties up to 450°C is observed after 3000h of test. The lowest value of the relative variation of solar absorptance for sample at 400°C measured at 2400h is probably due to a measurement error. The solar absorptance value after 2900h is near grow up to the initial measurement and the relative variation of solar absorptance is closed to 0%. Only the samples at 500°C show a degradation of the optical properties. After 1000h of test, solar absorptance decreases quickly and the emissivity rises at the same time.

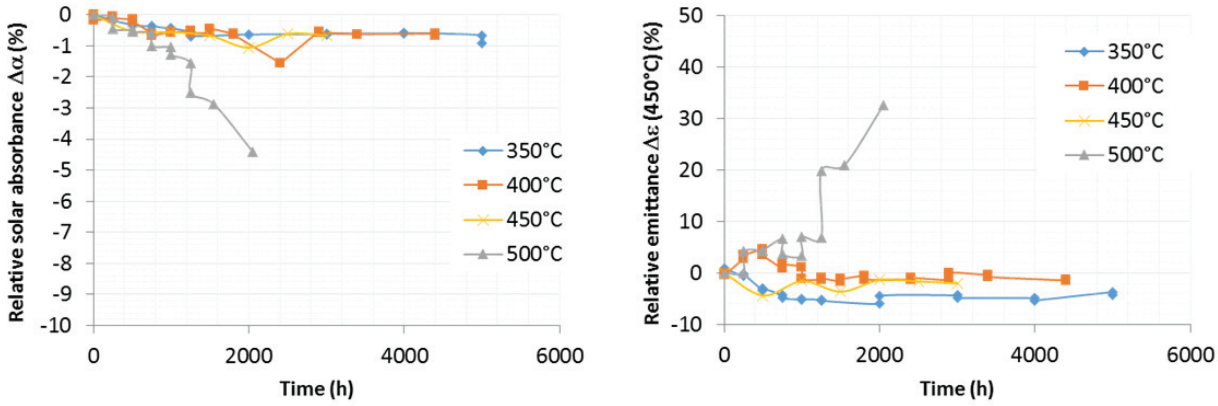

Fig. 3. Relative variation of total solar absorptance (left) and emittance at 450°C of sample as function of time for 350, 400, 450 and 500°C ageing

The solar absorptance is relatively stable for all ageing test up to 450°C. The relative degradation is less than 1%. No significant degradation of emittance was measured up to 3000h. At 450°C, the value of ε(450°C) grows from the beginning of the test with an acceleration after 750h. For other sample the emittance value remains constant or slightly decreases before getting stabilized. A calibration of our FTIR spectrophotometer was done during the test and corresponds to period around 750h of test. We observe that the measurement is not very stable with a poor reproducibility of emittance measurements. The emittance values were more reproducible after the calibration and correspond to the ageing time higher than 750h. We can conclude that only the sample at 500°C shows a significant variation of emittance and solar absorptance. Optical performances are stable after 3000h at 450°C, 4400 h at 400°C and 5000 h at 350°C.

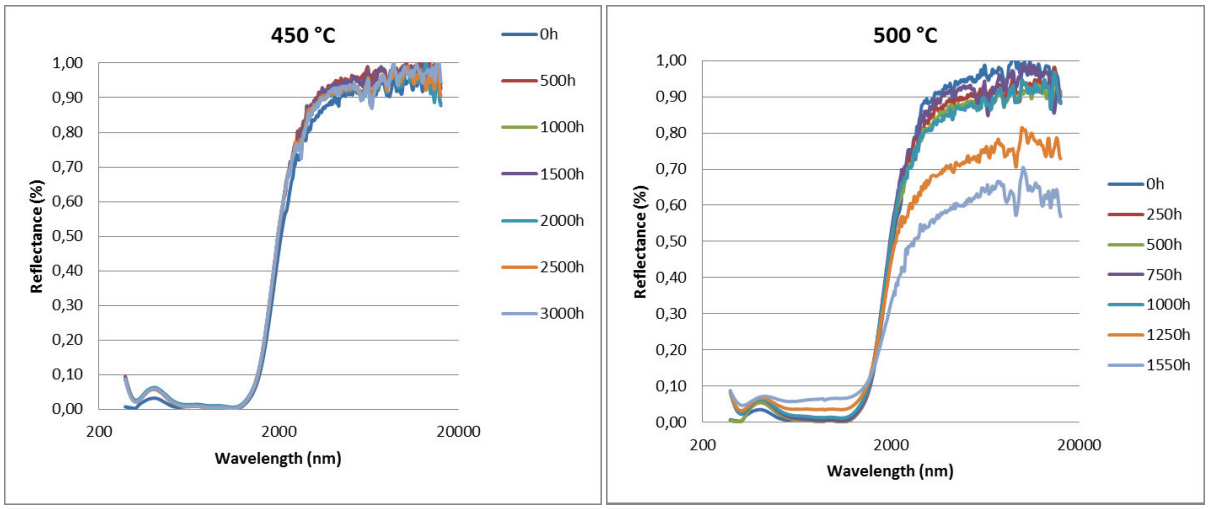

Fig. 4. Variation of the total reflectance spectra a function of time for ageing at 450°C (left) and 500°C (right)

Figure 4 shows the spectra of solar absorber as a function of time for ageing test at 450°C and 500°C. We observe that at 450°C no major variation of the total reflectance spectra appears up to 3000h. For sample at 500°C, reflectance in solar part of spectrum (between 280 and 2500nm) increased and decreased in the infrared part (between 2000 and 15000nm).

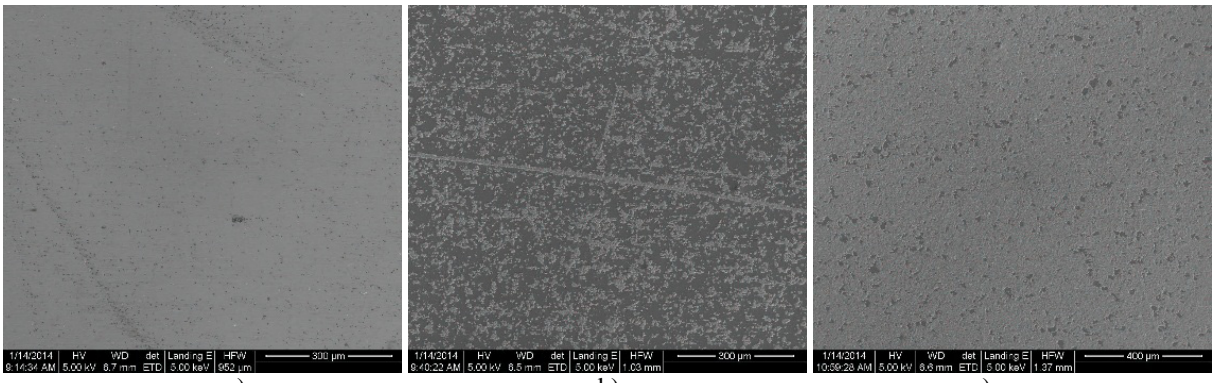

Fig. 5. SEM image of surface sample at t=0 (a), t=1250h (b) and 2050h at 500°C (c)

To understand what's happening on the coating during the ageing in temperature, the surface of the sample before and after the ageing has been observed. Thanks to optical microscopy, it can be seen that after 1250h at 500°C the surface of sample became irregular with apparition of structure like growing materials. The surface of the reference sample is smooth and very regular (see Figure 5). This modification of the surface is probably due to the oxidation of materials [4,5]. A SEM observation of surface confirms the hypothesis of a morphological modification of the materials. Figure 5 shows the image of surface of reference after 1250h and 2050h at 500°C. On the reference sample, surface is smooth and regular with small contrast probably caused by the Cermet layer above. On the aged samples we observe three dimensional structures all on the surface of samples. These structures appear when the solar absorptance starts to decrease at different points of surface. The density and the size of this defect grow as function of time and after 2050h cover all the surface of sample.

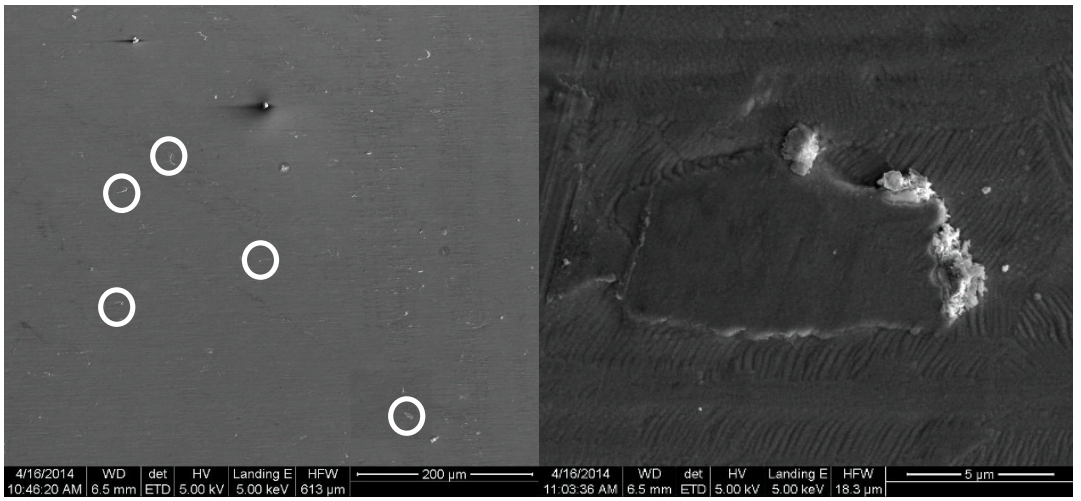

Fig. 6: SEM image of surface of sample after 3400h at 400°C. At left side, white circles indicate small cracks. Right side: zoom on a crack.

Fig. 6, a SEM picture of surface sample ageing at 400°C, shows a beginning in degradation after 3400h but without optical performances degradation. We observe small cracks on the surface with a beginning of growing of the same structures as observed at the higher temperatures. It is probably due to the beginning of the oxidation of metallic parts of the Cermet. The location of the defect is closed to the grain boundary of the top layer (antireflective

coating). The hypothesis of the degradation mechanisms is the diffusion of the oxygen through the grain boundary to the top layer, the expansion of the particles size from metal to oxide generates cracks on the top layer. The oxide materials continue to grow up from this defect to create the agglomerated structures observed on the surface. This observation shows that the degradation of materials has started but with no optical performances degradation. The density of defect is probably too low to affect the global measurement of the solar absorptance and emittance. However the ageing duration is too short to have a complete analysis of the degradation of this solar absorber. Data are not sufficient to calculate the activation energy of the degradation processes with an Arrhenius methodology [6,7]. So ageing tests should go on as to determine this energy. By this way and knowing the quantity of the oxygen inside the tube, lifetime of solar absorber could be determined.

Conclusion

The ASE solar absorbers have shown a good stability to the air oxidation. No variation of the optical properties has been observed after 3000h at 450°C, 3400h at 400°C and 5000h at 350°C. At 500°C the degradation of the optical properties has started after 1000h. Those results confirm the good resistance of the coating to the oxidation. At 400°C we observe in the SEM image a beginning of degradation after 3400h without modification of the optical performances. Small cracks appear on the top layer (antireflective coating) caused by the volume expansion of the oxidized cermet layer. Optical properties are expected to decrease with the ageing test pursuit. Ageing tests are to be continued up to observe optical variation for the four temperatures. By using an Arrhenius methodology we will be able to determine the activation energy of degradation mechanisms for this material. The final objective is to give a lifetime prediction for the stability of the coating in air at high temperature. This work shows a relatively good stability of the solar absorber from ASE in air at high temperature up to 450°C. As our knowledge it is a first time that a selective solar absorber with high performance (α>95% and $\varepsilon_{T=400°C}$<10%) shows a long stability in air at high temperature (up to 450°C).

Acknowledgements

The research leading to these results has received funding from the European Union Seventh Framework Program (FP7/2007-2013) under grant agreement n° 268219 “MATS” [8] and from French national funding from *Agence National de la Recherche* on the program *Investissements d’Avenir* (n° ANR-11-EQPX-0014) for some of equipment’s.

References

[1] C. Kennedy, Review of Mid- to High- Temperature Solar Selective Absorber Materials, Technical report, NREL (NREL/TP-520-31267), 2002.
[2] S. Esposito, A. Antonaia, M. Addonizio, S. Aprea, Fabrication and optimisation of highly efficient cermet-based spectrally selective coatings for high operating temperature, Thin Solid Films, 2009,517, 6000-6006.
[3] M. Köhl, B. Carlson, G. Jorgensen, A. Czanderna, A., Performance and durability assessment: Optical Materials for Solar Thermal Systems, Elsevier.2004
[4] A. Antonaia, A. Castaldo, M. Addonizio, S. Esposito, Stability of W-Al2O3 cermet based solar coating for receiver tube operating at high temperature. Solar Energy Materials and Solar Cells, 2010, 94(10), 1604-1611
[5] S. Cifuentes, M. Monge, P. Pãrez, On the oxidation mechanism of pure tungsten in the temperature range 600-800°C. Corrosion Science, 2012, 57, S. 114-121
[6] K. Gillen, R. Clough, Time-temperature-dose rate superposition: A methodology for extrapolating accelerated radiation aging data to low dose rate conditions. Polymer Degradation and Stability, 1989, 24 (2), 137-168
[7] M. Köhl; K. Gindele, M. Mast, Accelerated ageing tests of copper-oxide and Ni-MgF2-cermet solar absorber coatings. In: Solar Energy Materials, 1987, 16 Nr. 1-3, p 155 - 166
[8] MATS project web site: http://www.mats.enea.it/